

Arsenic Behavior Under Sulfate-Reducing Conditions:

Beware of the "Danger Zone"

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ABSTRACT

Throughout New England, naturally occurring arsenic is often present in groundwater at concentrations that exceed the new drinking water standard of 10 micrograms per liter. Although arsenic and other trace metals are ultimately derived from minerals in the underlying bedrock, these elements are subsequently redistributed through the glacial overburden by soil-forming processes. The geochemical mechanisms that control the partitioning of arsenic between soil and groundwater are complex and depend upon parameters that include pH and oxidation-reduction potential (ORP). Under oxidizing conditions, ferric iron oxide coatings on soil particles adsorb dissolved arsenic. Consequently, under high ORP conditions ($> +100$ mV), concentrations of arsenic in solution are usually low. When ORP is low (< -250 mV), sulfate in groundwater is reduced; iron, arsenic, and other trace metals may precipitate as sulfide minerals, and the associated aqueous concentrations again are low. In the "danger zone" between these extremes (ORP between -0 and -200 mV), the iron oxides and sulfide phases dissolve; any arsenic associated with them is released, and groundwater concentrations under these conditions may be as high as several thousand micrograms per liter.

Remediation strategies for dissolved arsenic or organic contaminants (e.g., chlorinated solvents) often drive significant shifts in ORP. Therefore, arsenic may be either dissolved or precipitated in conjunction with certain treatment technologies. Remedial design, as well as regulatory oversight, must consider these geochemical processes in order to avoid undesirable consequences. If an active remedy drives ambient redox conditions toward the "critical" range (e.g., -150 mV) from either direction, arsenic may be mobilized. Several examples from New England Superfund sites are shown, in which groundwater monitoring data validate this concern.

EXAMPLE 1. AOC-50

Groundwater beneath the former Moore Army Airfield (AOC-50), at the former Ft. Devens, central MA, is currently undergoing treatment for removal of PCE by an innovative, *in situ* process that drives redox conditions into the optimal range for reductive dechlorination (from approximately -150 to -300 mV). A pilot test at this site has successfully removed PCE, but lowering the redox potential of groundwater in the vicinity of the injection wells also created a groundwater zone containing high levels of dissolved arsenic (maximum 710 $\mu\text{g/L}$) and iron (maximum 490 mg/L) (Fig. 1). Early-time injections of dilute molasses solutions (Figs. 2 and 3) drove ORPs to extremely low values (e.g., < -400 mV) that were accompanied by low As and Fe; at higher ORP (around -150 mV), As and Fe reached maximum concentrations. Under ambient, oxidizing conditions (ORP $> +100$ mV), As and Fe in site groundwater are not detectable. The key process controlling As solubility under oxidizing conditions appears to be adsorption onto naturally occurring Fe oxyhydroxide coatings on the aquifer matrix. Under extremely reducing conditions, it appears that iron and arsenic precipitate, and the removal of sulfate from the system suggests that the formation of sulfide phases may play a critical role. The extent to which the kinetics of the key processes is affected by sporadic injections of a carbon source that also contains iron and sulfur is not known, nor are details of the low-ORP precipitation mechanism(s).

Full-scale implementation of the enhanced reductive dechlorination remedy for the PCE plume is currently under way. In recognition of the associated mobilization of arsenic to concentrations well above the MCL, performance monitoring is designed to address downgradient transport. In addition, recirculation wells have been installed to re-oxidize the groundwater so that elevated arsenic will be removed by adsorption, if necessary.

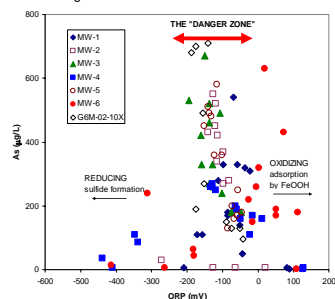


Fig. 1. Groundwater monitoring data from AOC-50.



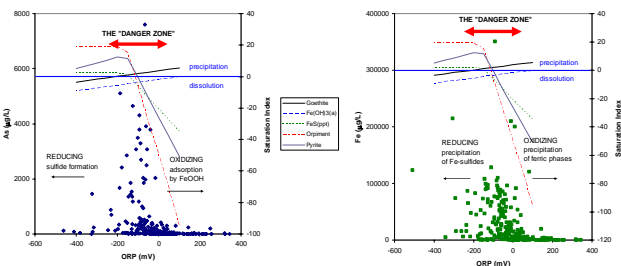
Figs. 2 and 3. Injection of molasses solution

EXAMPLE 2. Shepley's Hill Landfill

Shepley's Hill Landfill, also located on the former Ft. Devens, received domestic and military waste from the early 1900s until capping was completed in 1993. Surficial soils in the vicinity of the landfill consist of glacial sands and gravels, including peat deposits, and bedrock beneath the site is composed of gneiss and metasilstone containing sulfides. Deep groundwater beneath the landfill is high in dissolved arsenic and iron under moderately low-ORP conditions (between 0 and -200 mV) (Figs. 4 and 5). Beneath wetlands immediately downgradient from the toe of the landfill, ORPs are extremely low (< -200 mV) and iron and arsenic concentrations are low. Where more oxidizing conditions (ORP $> +100$ mV) prevail, iron and arsenic concentrations are low to non-detect. It is not known to what extent groundwater redox conditions are dictated by the composition of the overburden, or are influenced by contact with buried landfill waste. A significant volume of waste is located below the water table.

Because groundwater arsenic concentrations did not decline following installation of the landfill cap, a pump-and-treat interim remedy is under construction. The concern has been raised that the extraction pumping may cause a shift of redox subdomains, resulting in mobilization of arsenic. Of particular concern is the possibility that more oxidizing groundwater could move into a domain presently characterized by very low ORP and correspondingly low As. It is speculated that sulfide solid phases sequester As under strongly reducing conditions. Figures 4 and 5 show saturation indices for various Fe- and As-bearing phases, calculated using the geochemical equilibrium program PHREEQC and a typical Shepley's Hill groundwater composition. Where saturation indices (SI) are positive, solid phases are expected to precipitate; where SIs are negative, dissolution should occur. Above about 0 mV, oxides and oxyhydroxides are stable but dissolve as ORP decreases. SIs for the sulfide phases become positive around -100 mV and these phases are stable at ORPs below that value. These results are consistent with the observed peak in aqueous concentrations of both As and Fe (Figs. 4 and 5) around -100 mV.

Performance monitoring has been implemented to signal potential changes in downgradient redox conditions because a small perturbation in ORP can be accompanied by a large change in dissolved As concentration.



Figs. 4 and 5. Groundwater monitoring data from Shepley's Hill Landfill.

EXAMPLE 3. Grove Pond

Grove Pond is in Ayer, MA; a municipal water-supply wellfield is located on its south shore, adjacent to the former Ft. Devens. The aquifer is composed of over 100 ft of stratified glacial sands and gravels overlying metamorphic bedrock containing sulfide minerals. The supply wells are screened in a highly transmissive zone below 40 ft bgs; the overlying interval is characterized by higher silt content and markedly lower hydraulic conductivity. Correspondingly, groundwater in the producing interval is oxygenated (maximum ORP $+168$ mV) and low in dissolved iron and arsenic, while in the upper interval, groundwater is reducing (minimum ORP -200 mV) and iron and arsenic are high (maximum 21.9 mg/L and 189 $\mu\text{g/L}$, respectively) (Fig. 6). Bedrock groundwater exhibits extremely low ORP (minimum -401 mV) and low As (ND). There is no suggestion of any anthropogenic source(s) for the arsenic or influences on redox conditions at this site; the reducing zone in the overburden appears to be stratigraphically controlled (Fig. 7). Throughout the upper, low-ORP interval, As and Fe are strongly correlated due to reductive dissolution of ferric oxyhydroxides and release of sorbed trace metals. Pumping at the production wells appears to draw a small contribution of water from the upper reducing horizon, resulting in arsenic concentrations above the MCL in raw water. Subsequent treatment removes iron and manganese, as well as the arsenic, before the water enters the town's distribution system. Following the investigation of this wellfield, a recommendation was made to screen a planned new well deeper in the producing horizon in order to minimize "leakage" of water from the upper, low-ORP interval.

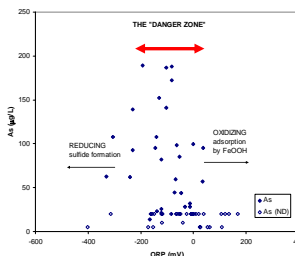


Fig. 6. Groundwater data from the Grove Pond arsenic investigation.

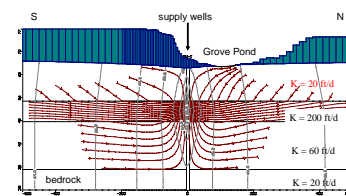


Fig. 7. MODFLOW simulation of groundwater flow to Grove Pond water supply wells.



Conclusions

Adsorption of arsenic by ferric oxyhydroxide surfaces and mobilization of arsenic by the dissolution of those surfaces under reducing conditions ("reductive dissolution") are naturally occurring geochemical mechanisms that often control arsenic behavior in groundwater. These processes are reasonably well-understood and well-documented. However, observations of low As concentrations under conditions that favor the formation of Fe and/or As sulfide phases are much less widely recognized. Anthropogenic perturbations to groundwater ORP, for example, due to active remediation (e.g., injection of a carbon source), landfill installation, or fuel releases, may either mobilize As from aquifer materials or sequester it through adsorption (oxidizing conditions) or sulfide precipitation (at very low ORP). Due to the complexity of the processes, number of variables, and high degree of uncertainty, extensive data are needed in order to characterize the "danger zone." Groundwater monitoring plans need to consider the appropriate sampling locations and analytes, in order to avoid – or at least to gauge the consequences of – driving ORP into this zone.

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